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Formation of Coordinated Nitrosamines by Reaction of K[IrCl$_5$NO] with Primary Amines

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Summary: In the present work we describe the formation of primary aromatic and aliphatic coordinated nitrosamines by reaction of the extremely reactive K[IrCl$_5$NO] with p-toluidine and 2,2,2-trifluoroethylamine, respectively. After the counteranion of the product was changed to tetraphenylphosphonium, crystal structures could be determined by X-ray diffraction. Complexes containing the highly unstable primary nitrosamines as ligands are generally scarce; moreover, to our knowledge this is the first example of isolated primary nitrosamines coordinated to a metal center through the NO moiety.

Primary nitrosamines (RN(H)N=O) and their tautomeric isomers, diazoic acids (RN=NOH), are important intermediates in the deamination of DNA bases[1] and in the formation of diazonium salts.[2] In acidic or neutral medium, these compounds rapidly produce unstable diazonium salts by loss of hydroxide ion.[3] Our group has previously explored the possibility of obtaining stabilized coordinated diazoates by reaction of nitrosyl complexes with aromatic and aliphatic primary amines,[4] a route previously explored by Meyer et al.,[5] who obtained coordinated aromatic diazonium salts. However, in the case of $[Fe(CN)_5NO]^{2-}$ and $[Ru(bpy)_2(NO)Cl]^{2+}$ with aliphatic amines only organic products derived from nucleophilic attack to the diazonium ion could be obtained (eq 1).[4] When $[M(CN)_5NO]^{2-}$ complexes (M = Fe, Ru, Os) was allowed to react with lithium *n*-butylamide, free (*E*)-*n*-butyldiazoate was found as the only product arising from the amide (eq 2). It was not possible to find appropriate reaction conditions to isolate the diazoate complex before labilization, even in the case of the inert osmium complex.[6] In the present work we describe the facile formation of an aromatic and an aliphatic coordinated nitrosamine (or diazoic acid) by reaction of the extremely reactive K[IrCl$_5$NO] with *p*-toluidine and *2,2,2*-trifluoroethylamine, respectively. Examples of complexes containing primary nitrosamines as ligands are generally scarce;[7] moreover, to our knowledge this is the first example of isolated nitrosamines coordinated to the metal center through the NO moiety.

$$ML_5NO + RNH_2 \rightarrow ML_5N(OH)N(H)R \xrightarrow{-H_2O} ML_5NNR \xrightarrow{Nu^-} ML_5 + N_2 + RNu \quad (1)$$

$$[M(CN)_5NO]^{2-} + BuNH^- \rightarrow [M(CN)_5N(OH)NBu]^{3-} \rightarrow [M(CN)_5]^{3-} + N(O^-)NBu + H^+ \quad (2)$$

The nitrosyl in K[IrCl$_5$NO] is probably the most electrophilic nitrosyl known to date. This fact is reflected by its extremely high IR frequency[8] and its electrochemical behavior;[9] both data show an excellent correlation with this property.

When *p*-toluidine or *2,2,2*-trifluoroethylamine was added to an acetonitrile solution of K[IrCl$_5$NO] at room temperature, immediate formation of the corresponding coordinated nitrosamine was observed as an orange precipitate. After recrystallization and change of the potassium counterion by tetraphenylphosphonium (PPh$_4$), crystals suitable for X-ray diffraction were obtained (Figures 1 and 2).[10,11] Relevant structural parameters for both compounds are shown in Table 1. Complete data are included as Supporting Information.

Three main facts are noticeable for these structures. First, according to the X-ray data, there is a proton close to N2 corresponding to the nitrosamine rather than the

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[8] KBr pellet: 2006 cm^{-1}, CH$_3$CN solution: 1953 cm^{-1}.

[9] $E_{1/2} = +0.96$ V vs Ag/AgCl in 1 M HClO$_4$. Compare with $E_{1/2} = -0.33$ V vs ferrocene in butyronitrile. Sieger, M.; Sarkar, B.; Zališ, S.; Fiedler, J.; Escola, N.; Doctorovich, F.; Olabe, J.; Kaim, W. *Dalton Trans.* **2004**, 1797−1800.

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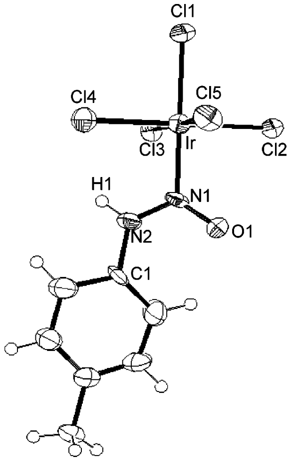

Figure 1. X-ray crystal structure and atom numbering for the anion portion of[$IrCl_5$(*N*-nitroso-*p*-toluidine)] (**1**). Thermal ellipsoids are drawn at the 50% level.

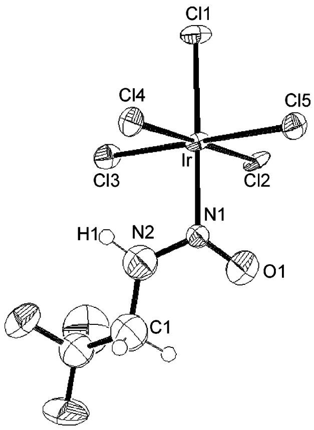

Figure 2. X-ray crystal structure and atom numbering for the anion portion of [$IrCl_5$(*N*-nitroso-*2,2,2*-trifluoroethylamine)] (**2**). Thermal ellipsoids are drawn at the 50% level.

Table 1. Selected Bond Lengths (Å) and Angles (deg) for 1 and 2

distance or angle	**1**	**2**
d(N1−N2)	1.309	1.32
d(N1−O1)	1.225	1.14
d(N2−C1)	1.455	1.47
d(N1−Ir)	1.992	2.020
d(Ir−Cl1)	2.383	2.352
d(Ir−Cl2)	2.353	2.356
d(Ir−Cl3)	2.365	2.358
d(Ir−Cl4)	2.362	2.368
d(Ir−Cl5)	2.336	2.354
d(N2−H1)	0.880	0.880
∠(N2N1O1)	118.4	120
∠(IrN1O1)	124.9	124.7
∠(C1N2N1O1) (dihedral)	4.9	−4

diazoic acid tautomeric form, indicating that at least in the solid state the nitrosamine is more stable. Second, they both correspond to syn compounds with respect to the RCH_2 and O substituents, while all known free diazoates are more stable in the *E* conformation.[12] Third, they are bonded to the metal through the NO moiety, while to our knowledge all known nitrosamines acting as nonchelating ligands are bonded to the metal center through the NH moiety. Concerning bond lengths in the ligands, there is a general similarity between both structures (Figures 1 and 2). We can mention as remarkable differences that the Ir−N bond is shorter and the NO bond is much longer in the case of the aromatic product (**1**) as compared to **2**, suggesting stronger back-bonding for **1** than for **2**. These facts are somewhat surprising to us, since the strong electron-attracting effect of the fluorine atoms should favor back-bonding in compound **2**, as observed in similar cases.[13]

The ^1H NMR spectra (see the Supporting Information) show in both cases a singlet attributable to −NH (or −OH) in the nitrosamine (or diazoic acid) at ca. 14.2 ppm for **1** and 13.1 ppm for **2**, suggesting a highly acidic character. We believe that this highly acidic character is responsible for the stability of these compounds, as compared with the corresponding free nitrosamines (or diazoic acids).[12] Free (*Z*)-diazoic acids tend to lose hydroxide rather easily in neutral and acidic solutions, while **1** and **2** are stable in aqueous neutral solutions and even in the presence of acids.[14] ^{15}N-labeled compounds with the moiety $Ir^{15}N(O)NR$ were obtained by reaction of $K[IrCl_5{}^{15}NO]$ with the corresponding amines, showing FTIR frequencies attributable to $N^{15}NO$ at 1428 cm^{-1} for **1** and 1534 cm^{-1} for **2**, as expected for the shorter N−O bond distance observed in the last case (see Table 1).

A proposed mechanism for the formation of **1** and **2** is shown in Scheme 1. Initial nucleophilic attack of the amine is followed by rapid deprotonation, producing the coordinated nitrosamines. Loss of water or hydroxide to produce a diazonium ion does not occur due, on one hand, to the stabilization of the nitrosamine form and, on the other hand, to the increased acidity mentioned above, both effects being produced by the $[IrCl_5]^{2-}$ moiety.

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(10) A 5.9 mg portion (0.055 mmol) of *p*-toluidine (dissolved in 0.25 mL of acetonitrile) for **1** and 1.8 μL (0.023 mmol) of 2,2,2-trifluoroethylamine for **2** were added under an Ar atmosphere at room temperature to 10 mg (0.023 mmol) of $K[IrCl_5(NO)]$ in 0.25 mL of acetonitrile. In both cases the orange product which precipitated immediately was separated from the solution by centrifugation (in both cases the counterions are the ammonium salt of the corresponding amine and a potassium ion; 98% yield in the case of **1** and 80% yield in the case of **2**). The tetraphenylphosphonium salts were obtained by adding a saturated aqueous solution of the crude product to an acetonitrile saturated solution of tetraphenylphosphonium bromide. After slow evaporation of the supernatant, the orange crystals so produced were separated by centrifugation and carefully dried. For more details see the Supporting Information.

(11) Crystal data for **1**: $C_{55}H_{48}Cl_5IrN_2OP_2$, $M_r = 1184.34$, specimen 0.8 × 0.2 × 0.05 mm, monoclinic, space group $P2_1/c$, $a = 10.706(2)$ Å, $b = 21.686(4)$ Å, $c = 21.956(4)$ Å, $\beta = 100.16(3)°$, $F(000) = 2368$, $V = 5017.1(17)$ Å^3, $T = 120(2)$ K, $Z = 4$, $D_c = 1.568$ Mg/m^3, $\mu = 3.033$ mm^{-1}, Refinement method: full-matrix least squares on F^2, $R = 0.0775$, $R_w = 0.0480$ (observed data with $I > 2\sigma(I)$). Crystal data for **2**: $C_{50}H_{46}Cl_5F_3IrN_2O_{2.5}P_2$, $M_r = 1203.28$, specimen 0.05 × 0.05 × 0.02 mm, triclinic, space group $P\bar{1}$, $a = 10.410(2)$ Å, $b = 10.731(2)$ Å, $c = 23.503(5)$ Å, $\beta = 91.70(3)°$, $F(000) = 1198$, $V = 2533.4(9)$ Å^3, $T = 120(2)$ K, $Z = 2$, $D_c = 1.577$ Mg/m^3, $\mu = 3.015$ mm^{-1}, Refinement method: full-matrix least squares on F^2, $R = 0.0860$, $R_w = 0.0652$ (observed data with $I > 2\sigma(I)$).

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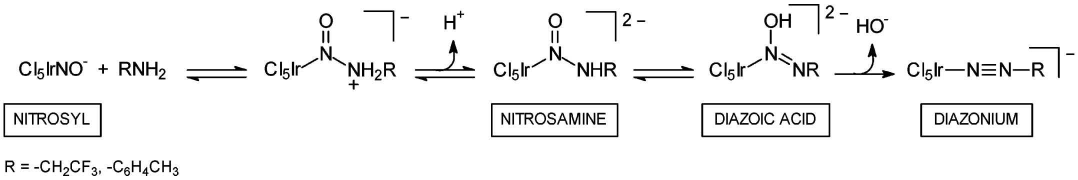
(14) Both compounds **1** and **2** are stable in water solution for several days. Decomposition could be observed only after addition of HCl(c), trifluoroacetic acid, or $HClO_4$(c), with an approximate half-life of 15 h at room temperature in all cases, compared to a few seconds or less for the free nitrosamines.[3]

Scheme 1



In summary, in this paper we have shown the facile formation of primary nitrosamines, bonded to the metal through the NO moiety in a rather unusual coordination mode. Differently from its free partners, the diazoates, the coordinated nitrosamines are stable even in the presence of strong acids. Moreover, this is the first direct evidence for the formation of coordinated primary nitrosamines by nucleophilic attack of primary amines at a transition-metal nitrosyl.

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Supporting Information Available: Tables giving complete crystallographic data and text giving experimental procedures and FTIR and NMR spectra; crystallographic data are also available as CIF files. This material is available free of charge via the Internet at http://pubs.acs.org.

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